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He was born on December 6, 1889. He went to the Protestant Gymnasium in Budapest and then studied mathematics and physics at the Philosophical Faculty of the University of Budapest. He graduated in 1912. Previously he had already been invited by Loránd Eötvös to the Geophysical Institute and after taking his degree he spent all the time he could spare working there. He took part in two geophysical expeditions, one of them was carrying out the determination of g on the ice of Lake Balaton and the other in Transylvania. The first world war interrupted his scientific career he served in the army from October 17, 1913-December, 1917. He was seriously wounded during the fighting on the Serbian battlefield. He obtained a degree as Ph. D. from physics in June 15, 1918. and received on October 1, 1923. the title of „Lecturer" of the Philosophical faculty of the University of Budapest on the base of his study on „Experimental and Theoretical Optics." During the time of his military service he even spent the short periods he was on leave at the Loránd Eötvös Geophysical Institute also dealing with optical problems besides gravitational investigations.

On October 1924. he became Professor of Experimental Physics of the University of Szeged.

In the meantime he had been granted a scholarship by the International Board of Education and went to the United States to continue his research work. He studied at the John Hopkins University at Baltimore and at the Physical Institute at the University of Chicago. In Baltimore he worked in the laboratory of Prof. R. W. Wood, in Chicago in those of Professors Millikan, Michelson and Compton. In 1928 he was delegated by the Hungarian State to continue his scientific research work at the Universities of Berlin, Jena, Göttingen, Heidelberg and Munich and in the same year the Hungarian Academy of Science elected him as a member. In 1930 the Institute of Experimental Physics of the University of Szeged was built and equipped according to his plans.

Initially he investigated classical optics, but during the period of his American scholarship he began to study questions concerning colloid phosphors. A token of the acknowledgement of his research work abroad was an appeal from Wo. Ostwald the Editor of the „Kolloid Zeitschrift" and one of the most prominent workers in this field inviting him to become a collaborator of the aforementioned periodical. His communications were also published in Annalen der Physik, Zeitschrift für Physik, Mathematikai és Természettudományi Értesítő and Math. és Fizikai Lapok.

As a man his dominating characteristic was his modesty, which reached such an extent that it even extended to his scientific work. Fame and glory were quite unimportant to him he worked for the sake of working not for personal ambitions, that is why he did not either stress the importance of his results.

As a research worker his work was characterized by great accuracy and precision. Before the publication of any paper he always carried out most precise control experiments and his collaborators had also to conform to this rule. He was a true physicist

who above all believed in experimental facts and was very careful concerning the explanations deduced from the experimental facts. He interpreted the experimental facts as simply as possible and advised his co-workers to act in a similar manner. In the case of a collaborator reporting on some partial result in the course of the experiments, he listened to him readily and even talked the matter over with him in detail, but if by any chance something diverging from the simple experimental facts was mentioned for instance: I believe this phenomenon will result in, then the answer was always: „it must be examined."

A significant part of his work was devoted to education. His lectures were exemplary, lucid and very comprehensible. He also directed his attention towards eliminating the dryness and monotony of the lectures by illustrating them with observations and anecdotes. He educated a whole generation who were all very attached to him and deeply moved by the event of his death.

His deeply human feelings and trend of thought was shown by the fact that he provided with equal kindness for all the members of his institute. He considered everybody to be his friend and as such tried to support them in every possible manner.

He died on October 15, 1949 quite suddenly under tragic circumstances. Unfortunately we could no more celebrate his 25 years jubilee as a Professor. Even during his brief illness — when he felt a little better — he sent for his co-workers and attempted till the very last to support them with his advice.

His death is an irreparable loss to his friends, co-workers, pupils and the University of Szeged.

The Scientific Research Work of P. Fröhlich

He began his scientific investigations with examinations concerning the field of classical optics. His earliest investigations were concerned with the examination of the polarization of the refracted ray in the vicinity of the critical angle of total reflection (1, 2). He examined the polarization state of refracted light rays at the critical angle of the total reflection. If the incident light ray is perpendicularly polarized to the plane of the incidence, i. e. the vector lies in the plane of the incidence, then a linear vector penetrates into the second medium which changes towards the direction of the normal of the separating plane.

The examinations strictly proved the theoretically established behaviour concerning the polarization of the refracted light ray.

He dealt in several papers in detail with one of the most important laws of classical optics with the limit of the validity of the geometrical law of reflection (3—7). In classical optics it has been theoretically established that the light vector penetrates also in the case of total reflection into the second medium. With the depth of the penetration the amplitude of the vector diminishes. Thus complete refraction can only occur if the thickness of the less dense medium is greater than the depth of the penetration of the vector. The ex-

perimental decision of the question is very difficult. Paul Fröhlich attempted to approach the problem from another point of view. The theory also leads to the conclusion that if the distance of the source of the light is the order of magnitude of the length of the light waves from the surface, the geometrical law of refraction is not valid.

This question was examined by P. Fröhlich. He elaborated an experimental method which enables the quantitative establishment of the deviation. Numerous detailed very accurate measurements were accomplished finally proving the expected results.

These earlier optical examinations concerned the completion of the knowledge of the most fundamental questions such as: the total reflection and the refractivity of light and achieved vital results.

In the middle of the third decade of this century Paul Fröhlich directed his attention towards the study of a very important branch of physics. He began to investigate structural problems by a significant method of investigation dealing with fluorescence and phosphorescence. This group of phenomena lead to very interesting and significant results, e. g. the conception that the emission of light is related to the return of the electrons to their original orbit in the atom was suggested for the first time in this connexion. P. Fröhlich continued his investigations in respect to luminescence without interruption till his death attaining very significant results in these studies which were also acknowledged by other investigators and also opened up new lines of approach for further research work. This paper can only give a very brief outline of his studies.

His examinations dealt with a characteristic group of the organic dye-phosphores with the gelatine phosphores. In the case of gelatine-phosphores the organic dye is firmly embedded in a rigid gelatine layer (10) and on excitation it fluorescences brightly giving with the Becquerel phosphoroscope a well visible phosphorescence.

The examinations concerning emission and absorption as well as excitation, decay etc. yielded many important results. According to Pringsheim and Vavilov the phosphorescence band is found always towards the long waves, consequently, particularly at low temperature, after the ceasing of the excitation a colour change in the long waves always takes place. Paul Fröhlich has shown (11, 12) that a colour change in the short waves can also occur and what is more, at certain temperatures, in particular cases, even a double colour change may take place.

Thus it could be proved that at certain temperatures the phosphor has two phosphorescence bands of different decay periods, one of which is found towards the short waves and the other towards the long ones, as compared with the fluorescence band. In connexion with this subject detailed examinations were carried out to elucidate the dependence of the phosphorescence band upon the temperature. (14, 15). It was demonstrated that the phosphorescence bands do not only depend in respect to their intensity, but also regarding their spectral distribution upon the temperature.

From the point of view of the dependence on the temperature

certain temperature optima occurred which varied entirely at the different bands of the same phosphor. The correlation between the individual bands and the optimal temperature, furthermore the relation to the concentration of the dye were determined by the analysis of the bands. Thus he established the importance of the concentration and temperature as regards the emission. He established which law governed the changes of the optimal temperatures and concentrations relating to the whole band complex of the phosphorescence.

In the course of their studies concerning emission Paul Fröhlich and Z. Gyulai (13) also discovered the phenomenon of the preexcitation effect, i. e. that the intensity of the emission is greater if the preparation is preexcited. At the subsequent examinations this phenomenon proved to be of great significance leading to highly interesting new establishments which will be described later.

Among the examinations relating to luminescence, the investigations dealing with the polarization of the emission are the most outstanding. On submitting the methods employed for the measuring of partial polarization to a critical survey a photoelectric method was worked out with the aid of which it succeeded for the first time to demonsrate that contrary to earlier conceptions the phosphorescence band is partially polarized pointing to the fact that the emission of its fluorescence, as well as its phosphorescence band, is a consequence of a unitary molecular mechanism. Within the emitting molecule the electron is anizotropic in respect to one axis also performing at room temperature thermal rotation. (10). In examinations carried out with liquid solutions he determined through the extent of the polarization of the fluorescence emission the dependence of the liquid upon the viscosity. He showed that in the case of different solvents with an identical viscosity the angle of polarization varies, hence a specific solvent effect can be established (8, 9). If the wave lengths of the exciting light increase, the angle of the partial polarization increases too. Examinations dealing with the phosphorescence emisson of solid gelatinous solutions of various dyestuffs led to the discovery of negative polarized emission (16, 17). It could be established that the angle of polarization could only be negative if the solid solution was cooled under a critical temperature, as otherwise in the temperature range characterizing negative polarization the range of polarization is a constant zero. The results obtained concerning polarization are in accordance with the theories of Perrin and Jablonski even supplementing them to a certain extent. It had to be assumed that with the changing of the temperature the angle made by the absorption and emission oscillator also changes and the smaller this change the more stable the structure.

The investigation of the partial polarization of the emission, as well as that of other questions relating to emission have led to the discovery that freezing and heating exert an influence on the structure of the preparation, however, the caused changes vary to a great extent. After heating, the preparation does not regain its original properties, whereas after freezing it usually behaves in the same manner as previously. It may be that the water which is removed under heating is the cause of this difference.

All studies have revealed that the manner in which the preparation is produced influences the properties of the solution to a great extent. In earlier investigations therefore, great care was taken that the method of preparation should be identical. Recently absorption measurements have enabled the determination of the factors influencing decisively the properties of the preparation in the course of the production. Thus it could be established that in relation to the absorption the initial concentration is the only essential factor, i.e. the concentration of the aqueous solution used for the preparation of the gelatine solution. This proved that an associated state exists also in solid solutions and that the ions participating in the absorption proceed unchanged from a liquid solution into a solid one, without being influenced by gelatine (21). Later it was shown that in the course of drying the associated state can slightly change, particularly if that process covers a longer period.

The analysis of the emission bands is rendered difficult owing to the phenomenon of self absorption, caused by the fact that the emission and absorption band intersect. The changes brought about by self absorption can be taken into account on the base of theoretical considerations. The equation obtained by virtue of theoretical calculations is in complete agreement with the experimental results (23).

The behaviour of dyestuff solutions was also investigated in an electric and magnetic field, however, a constant magnetic field did not cause an appreciable effect. A rotating magnetic field on the other hand, produces a constant change in the molecules of dyestuffs. This change could also be demonstrated with absorption measurements: in some cases a splitting of the band, in others a shift could be observed, detailed investigations concerning this matter are still in progress (20).

The further examination of the preexcitation effect described above led to the discovery of the quenching effect of preexcitation. Hence radiation with intensive light may not only effect an increase in absorption, but also its decrease. Recently both effects could be interpreted by virtue of a unitary molecular mechanism.

On the base of the theory of oriented light absorption the positive as well as the negative preexcitation effect can be explained. As in the same molecule a change of temperature may cause a positive preexcitation effect to change into a negative one, presumably in the same molecule the experimental conditions are the decisive factors determining whether normal or abnormal orientation is prevaling. This is a quite new result which has also been proved recently by another method (19, 22).

In order to afford a complete survey of the scientific research work of P. Fröhlich the results which have been enumerated in outline ought still to be supplemented with the results achieved by his collaborators and pupils as, of course, he promoted their investigations with his advice also giving them many new ideas.

Naturally these results cannot even be sketched in the frame of this paper. The investigations of P. Fröhlich, as well as those of his co-workers and pupils involved very extensive experimental material relating to the process of luminescence leading to

better understanding of this process. They contribute many significant factors to the progressive elucidation of the correlation existing between the different phenomena which could previously not be interpreted unitarily.

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Über den Einfluss von Lösungsmitteln auf die Extinktionskurven von organischen Verbindungen

Von Á. Kiss

Einleitung.

Es wurde wiederholt gezeigt, dass die Extinktionskurven von organischen Verbindungen von den Lösungsmitteln oft satark geändert werden. In dem Grade des Lösungsmitteleinflusses zeigen sich derartige Unterschiede, dass dipollose indifferente Lösungsmittel die Extinktionskurven sowohl von dipollosen, als von dipolhaltigen Verbindungen nur schwach ändern. Dementsprechend werden die in Hexan gemessenen Extinktionskurven bei der Untersuchung des Lösungsmitteleinflusses als Bezugsspektren gewählt.

Im Folgenden wird eine Systematisierung der wichtigsten idealisierten Wirkungsarten versucht. Übersichtlichkeit halber werden die Wirkungen von dipollosen, bzw. von dipolhaltigen Lösungsmitteln getrennt behandelt. Zwecks Abkürzung wird diesmal von der Angabe der reichen Literaturdaten abgesehen.

I. Die Wirkungsarten von dipollosen Lösungsmitteln.

Nach ihrer chemischen Zusammenseztung können sich die dipollosen Lösungsmittel indifferent, bzw. als wirkungsfähig verhalten. Indifferent sind gesättigte Verbindungen, welche keine Atome mit freien Elektronenpaaren enthalten. Wirkungsfähig können solche gesättigte, oder ungesättigte Verbindungen sein, welche Atome mit freien Elektronenpaaren besitzen.

A. Indifferente Lösungsmittel.

Wirkungsarten von dipollosen indifferenten Lösungsmitteln werden dadurch gekennzeichnet, dass hier zwischen den Molekülen des Lösungsmittels und denen des gelösten Stoffes keine Dipol-Wechselwirkungen auftreten können. Solche Wirkungen und Wirkungen anderer Art können zwischen den Molekülen des gelösten Stoffes sich ausbilden. Von den Eigenschaften des gelösten Stoffes abhängend können die folgenden Wirkungen auftreten:

a) Durch das Lösungsmittel werden die Extinktionskurven der gelösten Stoffe kaum geändert.

So verhalten sich die dipollosen gelösten Stoffe, da Dipol-Wechselwirkungen zwischen den Molekülen des Lösungsmittels und gelösten Stoffes nicht auftreten können.

b) Durch das Lösungsmittel werden die Kurven der gelösten Stoffe von der Konzentration abhängig geändert.

Auf diese Weise verhalten sich gewisse dipolhaltige Verbindungen. Die Ursachen können die folgenden sein:

1. Die Änderung des Assoziationsgrades.

Diese Wirkung kommt bei den dipolhaltigen gesättigten, oder ungesättigten Verbindungen mit freien Elektronenpaaren vor. Als Beispiel kann die Assoziation durch H-Bindung, welche in dipollosen Lösungsmitteln allgemein stärker ist, als in dipolhaltigen, gewählt werden.

2. Die Änderung des Assoziationsgrades.

Diese Wirkungen treten bei solchen Verbindungen basischen oder sauren Charaktres auf, bei welchen die Lichtabsorption im ionisierten und nicht ionisierten Zustand Unterschiede aufweist.

3. Die Dipol-Wechselwirkungen der gelösten Moleküle.

Mit diesen Wirkungen hat man bei dipolhaltigen gelösten Stoffen, bei grösseren Konzetrationen derselben zu rechnen.

B. Wirkungsfähige Lösungsmittel.

Die Wirkungen von dipollosen wirkungsfähigen Lösungsmitteln sind verwickelter Art, sie sind aber keine Dipol-Wechselwirkungen. Sie werden vor Allen durch die Eigenschaften der gelösten Stoffe bedingt. Eine Systematik der wichtigsten idealierten Wirkungsarten wird folgender Weise gegeben:

a) Die Kurven der gelösten Stoffe werden kaum geändert.

So verhalten sich die dipollosen Verbindungen, welche keine freie Elektronenpaare besitzen. Auf die Ursache wurde unter IAa hingewiesen.

b) Die Kurven der gelösten Stoffe werden konzentrationsabhängig geändert.

So verhalten sich die dipolhaltigen gelösten Stoffe. Vgl. die unter IAb angegebenen Wirkungsarten.

c) Die Kurven der gelösten Stoffe werden stark geändert.

Dessen Ursache ist die Koplexbildung zwischen den Molekülen des Lösungsmittels und des gelösten Stoffes. Dies kann vorkommen, wenn sowohl die Moleküle des Lösungsmittels, als die des gelösten Stoffes freie Elektronenpaare besitzen. Der Kürze wegen werden diese Wirkungen unter IIBc besprochen.

II. Wirkunsarten von dipolhaltigen Lösungsmitteln.

Die Wirkungen von dipolhaltigen Lösungsmitteln hängen davon ab, ob sie keine Atome mit freien Elektronenpaaren besitzen, bzw. solche enthalten. So ist an der Stelle, die Wirkungen beider Typen von Lösungsmitteln getrennt zu behandeln.

A) Wirkungsarten von Lösungsmitteln ohne freien Elektronenpaaren.

Die Wirkungen dieser Lösungsmittel hängen davon ab, ob die gelösten Stoffe dipollos, oder dipolhaltig sind, bzw. ob sie keine freie Elektronenpaaren besitzen, oder solche enthalten. In den zweiterwähnten Fällen sind die Wirkungen grösser, somit verwickelter Art. Die idealisierten Gränzfälle derselben können folgender Weise systematisiert werden.

a) Die Kurven der gelösten Stoffe werden nur schwach beeinflusst.

Auf diese Weise verhalten sich die dipollosen Verbindungen ohne freien Elektronenpaaren. Dessen Ursache ist, dass die Dipolfelder der Lösungsmittelmoleküle die Ladungsverteilung der Elektronen der gelösten Moleküle induktiver Art nur schwach beeinflussen. Die Folgen dieser Wirkungen können sein:

1. Die Extinktionskurve, bzw. gewisse Banden derselben werden nach den kurzen, bzw. langen Wellen verschoben.

Dies wird durch die Erhöhung, bzw. Herabsetzung der Anregungsenergie verursacht.

2. Die Extinktion wird geändert.

Dessen Ursache ist, die Änderung der Übergangswahrschenlichkeit.

3. Die Schingungsstruktur der Banden wird verwischt.

Dies kommt davon, dass die gelösten Moleküle in verschiedenem Masse polarisiert werden.

b) Die nicht lokalisierten Dipol-Wechselwirkungen beeinflussen die gelösten Moleküle vorwiegend induktiver und mesomerer Art.

Wirkungen dieser Art können bei dipolhaltigen Verbindungen ohne freien Elektronenpaaren vorkommen. Diese Wirkungen äussern sich auf folgender Weise:

Die unter IIAa erwähnten Wirkungen zeigen sich in grösserem Masse.

c) Die Dipol-Wechselwirkungen teils lokalisierter Art beeinflussen die Kurven der gelösten Stoffe stark.

Diese Wirkungen zeigen sich bei dipolhaltigen Verbindungen mit freien Elektronenpaaren. Die Erscheinungsformen der Wirkungen können sein:

1. Die unter IIAb erwähnten Wirkungen.

2. Die Anlagerung von Lösungsmittelmolekülen an die reaktionsfähige Atome der gelösten Verbindungen.

Der Kürze Wegen werden die Folgen dieser Wirkungen unter IIBc besprochen.

B) Wirkungsarten von Lösungsmitteln mit freien Elektronenpaaren.

Die Wirkungen dieser Lösungsmittel hängen von den Eigenschaften der gelösten Verbindungen unter IIA angegebener Weise ab. Die folgenden idealisierten Gränzfälle der Wirkungen können unterschieden werden:

a) Die Extinktionskurven der gelösten Verbindungen werden nur schwach geändert. Diesbetreffend vgl. IIAa.

b) Die nicht lokalisierten Dipol-Wechselwirkungen beeinflussen die Elektronenverteilung der gelösten Moleküle induktiver und mesomerer Art. Diebetreffend vgl. IIAb.

c) Die Dipol-Wechselwirkungen vorwiegend lokalisierter Art beeinflussen stark die Kruven der gelöstem Stoffe.

Mit diesen Wirkungen hat man bei dipolhaltigen gelösten Stoffen mit freien Elektronenpaaren zu rechnen. Die Bindung von Lösungsmittelmoleküle führt zur Bildung von Komplexen den stöchiometrischen Gesetzen entsprechend. Die Wirkungen dieser Vorgänge zeigen sich folgender Weise:

1. Die Komplexbildung unterbricht die Mesomerie des angegriffenen Atoms.

Dadurch wird die Extinktionskurve, bzw. die betreffende Bande derselben nach den kurzen Wellen Verschoben und die Extinktion nimmt ab.

2. Die Komplexbildung stabilisiert die polare mesomere Grenzform des gelösten Moleküls.

Die Folge davon ist, die Verschiebung der Extinktionskurve, bzw. deren erste Bande nach den langen Wellen und die Zunahme der Extinktion.

3. Die Komplexbildung ermöglicht neue Mesomeriefälle.

Dadurch wird die Struktur der Extinktionskurve verändert.

4. Durch die Komplexbildung entsteht ein einheitliches System von π-Elektronen

Dadurch wird die Extinktionskurve, eventuell unter gleichzeitiger Strukturänderung nach den langen Wellen verschoben.

5. Die Komplexbildung wird durch chemische Reaktionen begleitet.

Dadurch wird die Struktur der Extinktionskurve verändert. Eventuell kann der zeitliche Verlauf der Extinktionsänderung befolgt werden. Als Beispiel kann die Halbazetal, bzw. die Hydratbildung bei den Aldehyden und Ketonen erwähnt werden.

Allgemein kommen die erwähnten Effekte nicht rein, sondern gemischt vor. Versuche sind im Gange um die Brauchbarkeit dieser Systematisierung zu zeigen.

Szeged (Ungarn) Juli 1949.

On Newton's Laws of Motion

By K. Szėll

The classical mechanics, founded by Galileo and Newton, developed by many famous mathematicians and physicists is a logically self-consistent and fundamental part of physics. The science of mechanics rests primarily upon the three Newton's laws of motion:

I. Every body continues to be in a state of rest or of uniform motion in a straight line unless it is compelled by force to change that state.

II. Change of motion is proportional to the force applied and takes place in the direction in which the force acts.

III. To every action there is an equal and opposite reaction, or the mutual reactions of two bodies are equal and opposite.

I show in the following lines that Newton's laws of movement are synthetic judgements which can easily be proved by the aid of the law of cause, on the base of dialectical materialism.

Faith in the exterior world, independently from the observer, is the base of natural science. Every knowledge assumes a subject (who perceives something) and an object (which is perceived). The objects of the exterior world produce pictures in us, which we construct by the action of contemplation and intellect. The causal relation is the condition by which we acknowledge something to be existing, i. e. that we accept it as an object. According to the law of cause therefore whatever brings about a change in us exists for us. Furthermore it also means that every happening has a cause. The law of cause is the law of change, it is therefore not the law of the origin of existence and so only the cause of change can be sought for.

The laws of nature are always composed of two factors. The one factor being action and the other contemplation. The action occurs on the base of the law of cause, contemplation applies to the empirical elements needed for perceiving nature.

I. Direction belongs to the conception of movement it is given by the spacial direction of the action. If there is no exterior cause the direction of the action does not change, the body always proceeds in the same direction. On the other hand, if an exterior cause is lacking the $s/t = v$ velocity equation is constant. This equation establishes an intellectual factor derived from the quotient of our two contemplations. The first law of movement can therefore be justified by the lack of cause. *This first law is a synthetic judgement based on experience.* The investigators who state that the first law *cannot be justified on the base of experience,* draw this conclusion from an entirely mathematical point of view[1]. We must choose the frame of reference in such a manner that this law should be valid.

II. Newton's second law is the definition of force. In the second law „motion of a body" means mass of the body × its velocity and the change of motion means the rate of change of momentum with respect to time. Assuming that the mass remains constant.

$$\frac{d}{dt}(\text{mass x velocity}) = \text{mass x acceleration}$$

This equation does not tell what force is. It merely says that forces are measured by the accelerations with which they are associated.

In the pictures of the objects the sensual data do not point toward the cause. On the pictures there is no such feature which would define them as cause or effect. The causal relation joins the sensual data on the base of the logical arrangement of the pictures. The establishment of the cause and effect expresses a synthesis which is produced by the observer (the subject) on the base of experience.

Consciousness takes up a casual relation because it remarks a change. Of two objects we define as effect the one which has changed, the constant one (if it is also only relatively so) we consider as cause. For the intellect the constant is the cause and the variable the effect. Logically the cause must be prior to the effect. This is, however, not a time but a logical priority. Therefore the action, the force is the cause, the acceleration the effect.

[1] Cf. A. Voss, Encyklopädie der Mathematischen Wissenschaften, IV, 1. pp. 54. „.... Überdies, ist es eine Täuschung, wenn man glaubt, dass sich in der Erfahrung dasselbe (das Trägheitsprinzip) nachweisen lasse. Allerdings lässt sich erkennen, dass die Abweichungen von der Trägheitsbahn kleiner und kleiner werden, je mehr man gewisse die Bewegung beeinflussende „Umstände" beseitigt; dass aber, wenn der Punkt sich gleichförmig und geradlinig bewegt, solche Umstände nicht mehr vorhanden sind, wird schon vorausgesetzt und liegt jenseits aller möglichen Erfahrung... Man kann sich daher sehr wohl eine Mechanik denken, bei der die Bewegung des unbeeinflussten Punktes eine ganz andere wäre, so z. B. F. Reech im Cours de mécanique, vgl. Fussn. 72; dann J. Andrade, Mécanique physique; ähnlich äussern sich auch H. Poincaré und P. Panlevé. Revue de métaphys. 8. 5. (1900) pp. 557; auch schon weit früher Jacobi in seiner Vorlesung 1847/48, p. 1."

Mac Millan draws conclusions from a purely mathematical point of view. I quote from his book „Theoretical Mechanics, Statics and the Dynamics of a Particle" (1927) p. 37.: „It will be observed that Newton's second law says nothing about causation. Since the force and the acceleration are simultaneous, there is no more reason for asserting that force is the cause of the acceleration than for asserting that acceleration is the cause of force. The fact that force is commonly spoken of as the cause of acceleration merely shows that in order of our thoughts, force is commonly placed before acceleration. In the philosophical sense, nothing is known about causation". In his establishments on acceleration Mac Millan did not take into consideration logical priority so that his assertions cannot be accepted. There is an essential difference between the purely mathematical point of view and the physical content of the law.

If there is no exterior action it ensues from the force equation: mass x acceleration that the velocity according to its magnitude and direction is constant. Therefore the second law of movement also involves the first one, which is a generally accepted fact.

III. In the third law the words *action* and *reaction* are to be understood as forces. Action is the cause, reaction is the effect. They are equal in magnitude and opposite in direction. Logically three cases are possible:

1. The magnitude (A) of the force of cause is greater than the magnitude (B) of the force of effect: $A > B$. 2. $A = B$. 3. $A < B$.

If A is greater than B, then the cause would comprise such a factor which did not contribute to the effect.

If A smaller than B, then B would comprise such a factor which does not ensue from the cause.

It is therefore necessary that $A = B$ that is the effect is equal to the counter-action. As the reaction appears as a resistane its direction is in opposition to the action.

To Newton's three laws of movement, to the axioms there is still attached a fourth according to which the forces are to be added as „vectors". On the base of Newton's mechanics, Newton's second law of movement contains this. Generally forces from different directions are to be added on the base of the parallelogram thesis, logically this ensues from the multiple cause thesis.

The laws of movement are often also called axioms. As, however, the denomination axiom signifies a thesis which cannot be proved, the denotation: laws of movement is more appropriate.

Mitteilung aus dem Institut für Experimentalphysik der Universität Szeged

Über die Leitungsart der Gelatine-Farbstoffphosphore

VON LAJOS GOMBAY

Die Leitfähigkeit der festen Gelatine-Farbstoffphosphore wurde in bezung auf's Ohms'che Gesetz (1) bei gleichmässiger Temperaturänderung, höherer und niedrigerer konstanten Temperatur (2), Vorströmen bei Zimmertemperatur (3), Entwässerung bei Vakuum-Behandlung (3), und bei Erhitzung (4), und bei Änderung des Polarisationsstromes (5) untersucht.

Es ist bemerkenswert, dass die Gelatine-Farbstoffphosphore während der Wärme- und langwelligen Lichtabsorption bei elektrischen Strömen eine neue elektromotorische Kraft zeigen. Dies Ergebnis kann man so deuten, dass eine Aufladung in den Gelatine-Farbstoffphosphoren entsteht, die sich im Polarisationsstrom wieder rückgänging macht. Dieser Prozes zeigt uns auch die Veränderung der Struktur der Gelatine-Farbstoffphosphore. Da die Gelatine-Farbstoffphosphore aus heteropolaren Micellargitter-Bruchstücken bestehen, könnte man sagen, dass die Kolloidteilchen unter der Wirkung der Energieabsorption abgebaut werden, und auf diese Wiese ensteht eine feinere, stabilere Gitterstruktur.

Unter den Eigenschaften der Gelatine-Farbstoffphosphore ist ein Widerspruch scheinbar. Nämlich auf die Gelatine-Farbstoffphosphore ist das langwellige Licht sehr wirksam, doch hat der Gelatine-Farbstoffphosphor eine kurze lichtelektrische langwellige Grenze. Um diese Umstände deuten zu können, ist es zweckmässig die elektrische Leitungsart zu bestimmen.

Bis jetzt wurde nur die metallische Leitung vermutet (6), ob auch eine elektrolytische Leitung vorhanden ist, blieb noch unentschieden. Die Schwierigkeiten waren gross, weil die Leitfähigkeit der Gelatine Farbstoffphosphore sehr gering ist. Darum legte ich 250 Volt Spannung auf die Gelatinefolien. Die zur Untersuchung gebrauchten Gelatinephosphorfolien waren 10 mm lang, 10 mm breit und 0.1 mm dick. Die Konzentration der festen Gelatinphosphore war $10^{-1}-10^{-3.5}$ gr Rhodulin Orange N/cm³ trockene Gelatine und auch leere Gelatine. 20 Tage lang wurden die Folien vom Strom durchflossen. Dann wurden einige Mikrophotographien der von dem Strom durchgeflossenen Folien aufgenommen.

Fig. 1. zeigt das Bild eines positiven Pols und Fig. 2. solches eines negativen. Es ist ersichtlich in Fig. 1., dass Materie sich am positiven Pol anhäufte.

So scheint es, dass die Wanderung erstens im kolloiden Zustand geschieht, die in Fig. 1. aus den dunkleren Bändern ringsum an den ganz dunklen Flecken ersichtlich ist. Später werden die Kolloidkörnchen um einen Kondensationsmittelpunkt zusammengehäuft. So bilden sich dei kleinere Körnchen aus. Bei der weiteren Ausscheidung werden sich diese kleineren Körnchen zu einem makroskopischen Korn vereinigen, das man am Ende des positiven Pols auch mit freiem Auge sieht.

Fliesst der elektrische Strom noch längere Zeit (beiläufing 30 Tage), durch die Folie, dann erschaffen die einzelnen Körner eine zusammenhängende Schicht an dem positiven Pol, wie Fig. 3. ersichtlich ist.

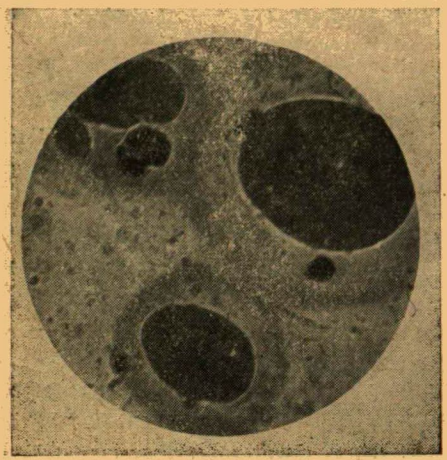

Fig. 1.

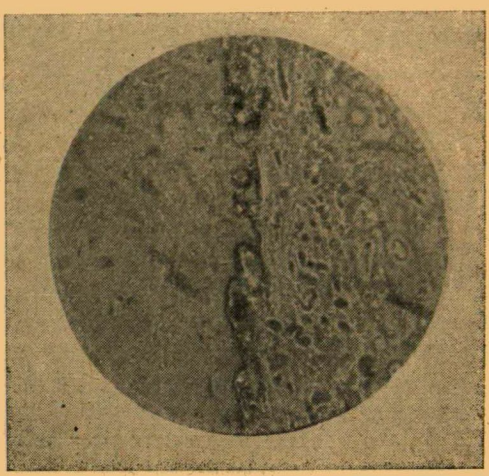

Fig. 2.

Fig. 2. zeigt uns, dass Materie von dem negativen Pol abgewandert ist, darum sieht man die kleineren, helleren Flecken unter der Kathode. Zwischen den beiden Elektroden sieht man keine Änderung, weil da sowohl die Materiewanderung, als auch der Strom stationär sind.

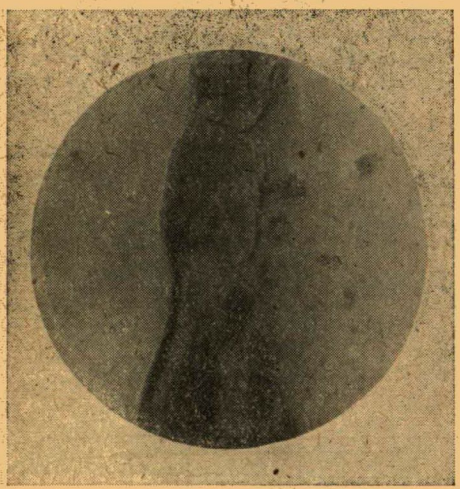

Fig. 3.

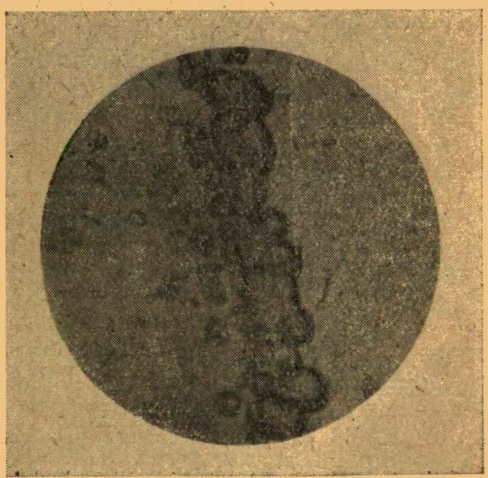

Fig. 4.

Auch das muss bemerkt werden, dass man die Zusammenhaufung der Materie an dem positiven Pol der leeren Gelatine beobachten kann. Aber in Fig. 4. sieht man, dass die Ausscheidung der

Materie bei leeren Gelatine veil geringer ist, als die bei dem Gelatine-Farbstoffphosphor. Aus diesem Messergebniss kann man folgern, dass die bei dem Gelatine-Farbstoffphosphor ausscheidende Materie auch bei der leeren Gelatine abwandernde Materie enthält. Man kann so annehmen, dass die Bruchstücke der leeren Gelatine die primär wandernde Materie sind, und in diese ist der Farbstoff der Gelatine-Farbstoffphosphore hineingebaut, der bei der elektrolytischen Leitung zu der Anode wandert.

Aus diesen Messergebnissen kann man folgern, dass negative Ionen mindestens in diesen Gelatine-Farbstoffphosphor (Rhodulin Orange N und auch leere Gelatine), unter der Wirkung einer äusseren Spannung zu der Anode wandern. So ist es verständlicher, dass während des Primärstroms eine grosse elektrische Auflandung im Gelatine-Farbstoffphosphor vorhanden ist, die sich im Polarisationsstrom zurückbildet.

Die elektrolytische Leitung und die mit dieser verbundenen Aufladung stellen klar, dass die lichtelektrische Empfindlichkeit (7) der Gelatine-Farbstoffphosphore eine kurze rote Grenze hat, obwohl die langen Lichtwellen eine grosse Wirkung auf diese Farbstoffphosphore ausüben. Nämlich die Primärströme (8) können nur dann stationär fliessen, wenn sie in dem Gitter keine bleibende Veränderung machen. Hier fliesst mit dem Elektronenstrom gleichzeitig auch der elektrolytische Polarisationsstrom um diese verändern die Gitterstruktur des Gelatine-Farbstoffphosphors, weil eine Auflandung in den Gelatinefolien ensteht. die das lichtelektrische Strömen bei den längeren Lichtwellen — die eine kleinere Energie haben — verhindert. So ist es klar, dass die lichtelektrische rote Grenze der Gelatine-Farbstoffphosphore nur unter dem 300 $m\mu$ liegt.

Es ergeben sich kurz zusammengefasst folgende Resultate: der Gelatine-Farbstoffphosphor ist ein metallischer und gleichzeitig auch ein elektrolytischer Leiter d. h. ein gemischter Leiter und aus dieser Tatsache folgt auch die kurze rotwellige Grenze des lichtelektrischen Effekts.

Vorliegende Arbeit wurde im Institut für Experimentalphysik der Universität Szeged vollendet. Für die vielseitige Beihilfe und für die freundliche Anregung möchte ich auch an dieser Stelle Herrn Prof. Paul *Frőhlich* herzlichst danken.

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Institute of Experimental Physics

Further Investigations on the Saturation of Gelatineous Dyestuffs

By L. Szalay

Introduction.

By using a constant exciting light the intensity of phosphorescence emission increases after initial excitation till it reaches a maximum. This phenomenon is termed saturation of phosphor. This saturation means that every molecule which can be excited by a given intensity of exciting light, is in an excited state and that the number of molecules entering this state during the unit of time, are identical to the number of emitting molecules.

Investigations concerning saturation have shown (1) that the phenomenon of saturation itself as well as the phenomena connected with it may be interpreted by assuming the orientation of molecules. Molecules are only excitable if their plane is normal to the beam of the exciting light. The molecules orientate under influence of irradiation, i. e. their planes take up the suitable position for excitation. Since the molecules deviate in a different manner from the oriented condition, the time required for single molecules to reach this oriented state is also different. The saturation is an orientation effect, and the time required for saturation is identical with the duration of the orientation.

On studying preexcitation, which necessitated further investigation of saturation, P. Fröhlich and L. Szalay (2) observed an interesting circumstance. They demonstrated that the positive preexcitation effect corresponds to normal orientation, and the negative preexcitation to that an of the abnormal one. (Concerning abnormal orientation see (3)). According to their results less energy is required for abnormal orientation, consequently the optimal concentration of the negative preexcitation effect is to be found at greater concentrations, than that of the positive preexcitation effect. It was further shown that the orientation increases with decreasing concentration. Regarding particulars of saturation and preexcitation see previous papers (1, 2, 4).

Since saturation is due to the orientation effect, it is important to investigate minutely the influence of temperature on saturation, partly to ascertain how far the above mentioned opinion concerning normal and abnormal orientation proves to be correct and partly because it is to be hoped that hereby further informations regarding the effect of orientation may be obtained.

Experimental method.

The experimental method was the same as adopted for previous investigations (1). The space between the discs of the Becquerel phosphoroscope could be electrically heated in order to obtain higher tempereatures. Low tempereatures were produced by solid CO_2. For details on the phosphoroscope which can be heated and

cooled see previous papers (3). By using solid CO_2 a temperature of — 30° C could be obtained in the measuring space. Because of the deformation of gelatine plates, measurements above + 110° C were impossible.

For the measurements which were made by the method of P. Fröhlich (6). Gelatine plates of 0,1 mm thickness were used. The examined dyestuff was acridine orange N. The concentrations were logarithmic.

Results.

The duration of saturation of the dyestuff plates was established at the temperatures of + 110° C, + 55° C, + 28° C and — 30° C respectively. Table I. shows the results of these measurements.

Table I.

Temperature °C	concentration — c								
	1,00	1,50	1,75	2,00	2.25	2.50	3,00	3,25	3,50
	duration of saturation in seconds								
—30	31	19	—	13	—	12	18	29	38
+28	21	17	14	11	19	13	29	43	71
+55	14	11	9	10	13	—	40	61	—
+110	10	7	7	11	17	25	75	—	—

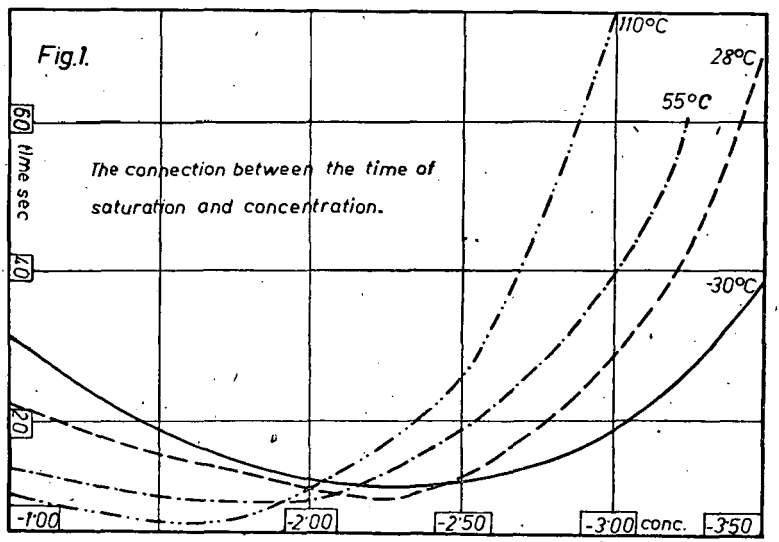

Fig. 1. was delineasted by using these data. Fig. 1. illustrates clearly the connection between duration of saturation, temperature and concentration. The logarithmic concentration was measured on the horizontal axis, and the time of saturation in seconds on the vertical one.

The object of these experiments was the further elucidation of the orientation effect of molecules; for this reason temperatures

were selected proving from the point of view of orientation to be important for the acridine orange dyestuff. Preexcitation was without effect at a temperature of $+28°$ C, thus any permanent orientation at this temperature cannot be assumed, or even if it would occur the desorientating effect of the moderate measuring light would destroy it. The optimum of the negative preexcitation effect was found at $+55°$ C, consequently the optimum of abnormal orientation must also exist at the same temperature.

Fig. 1. shows that the duration of saturation has an optimal concentration at every temperature. The optical concentration shifts with increasing temperature to greater concentrations. The optimal concentration amounts to $-2{,}5$ at $-30°$ C, and to 1,50—1,75 at $+110°$ C. There exists a concentration — between $-2{,}00$ and $-2{,}25$ — where the duration of saturation is the same at every temperature. From this concentration towards greater concentrations the duration of saturation increases at decreasing temperature, while at smaller concentrations the duration of saturation diminishes with decreasing temperature.

It is to be noted that the method of measuring the duration of saturation revealed an interesting phenomenon. After removal of the screen the time which was necessary to eliminate the difference between the emission of the saturated and unexcited plate-parts was measured. This is termed the duration of saturation. It could, however, be observed, that the concealed plate-part, which had been kept in darkness, was not uniformly saturated after removal of the screen. First the sharp line, which was produced by the removal of the screen and which separated the dark and light surfaces faded; proceding from this line to the border of the plate the concealed plate-part became saturated. Since the surface of the plate was perfectly uniformly illuminated, the marked progress of the saturation from the centre of the plate towards its rim can only be explained by assuming the existence of self-excitation. The light of the emitting molecules arranged on one side of the separating line excite the unexcited molecules in their immediate vicinity.

In principle self-excitation is not impossible for the absorption and emission spectra mutually cross. However, its effect is so small, that it cannot be revealed by usual methods. An attempt to establish self-excitation in a direct manner is in progress.

Discussion.

Considering the process of saturation as a process of orientation of molecules the results of saturation may be interpreted on the base of the hitherto achieved results as follows:

1. The optimal concentration.

As regards saturation an optimal concentration can be found at a certain temperature at which the saturation is completed in the shortest time. From this concentration on more time is needed for the saturation of preparations in the case of all other concentrations. As was mentioned above the process of saturation is the process of the orientation of the molecules. The capacity of the molecules to orientate increases with decreasing concentrations (2); similarly also the absorption increases and with it the emissivity. Thus the duration of saturation ought to diminish with decreasing

concentration. The development of an optimal concentration cannot be satisfactorily explained for the present.

2. The shifting of optimal concentration.

The optimal concentration shifts towards greater concentrations with increasing temperature (2). According to the investigations about preexcitation (4), preexcitation has no effect at +28° C. Thus permanent orientation is inconceivable. But even if permanent

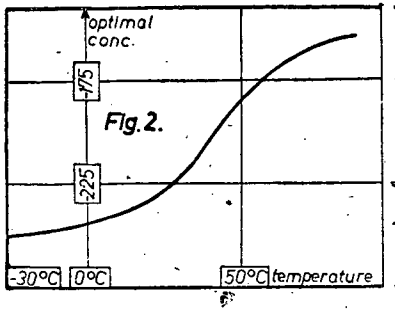

Fig.2.

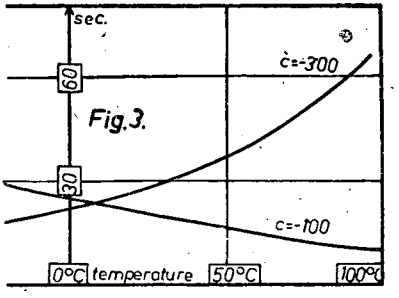

Fig.3.

orientation should exist, the desorientating effect of the moderate light used for measuring would eliminate it. At this temperature the optimal concentration concerning the saturation was — 2,25 which corresponded to the previous results relating to other phenomena (7). From +28° C onwards the orientation effect was normal, and towards higher temperatures it was abnormal. Since less energy was required for negative preexcitation, thus also for abnormal orientation, the optimal concentration from the point of view of the duration of saturation shifted to greater concentrations. Similarly, the optimal concentration as regards the negative preexcitation effect, is greater than the optimal concentration of the positive preexcitation effect. This shifting of the optimal concentration is caused by the slighter disturbing effect of the neighbouring molecules in the case of abnormal orientation (2).

3. There exists a concentration at which the duration of saturation is the same at every temperature.

The curves representing the duration of saturation intersect in one point within the limit of error (Fig. 1.). This denotes that at a concentration of about —2,25 the duration of saturation is independent of the temperature. Thus the same energy is required to produce both normal and abnormal orientation at a concentration of —2,25. Comparing the correlation between the duration of saturation and the temperature at greater concentration (i. e. —1,00) we find that the duration of saturation increases with decreasing temperature (Fig. 3.). This means that at greater concentrations more energy is needed for normal, than for abnormal orientation. On investigating how far the duration of saturation depends on the temperature at smaller concentrations (i. e. —3,00) we find that the duration of saturation decreases with diminishing temperature (Fig. 3.). Since abnormal orientation changes with decreasing temperature into normal orientation, it is evident that at smaller concentrations more energy is required for abnormal orientation.

Considering that the optimal concentration of the positive preexcitation effect is smaller than that of the negative preexcitation

effect, these results can be easily explained assuming that normal orientation corresponds to the positive, and abnormal to the negative preexcitation effect.

Thus it is also obvious that there exists a concentration at which the duration of saturation does not depend on temperature. At small concentrations abnormal, at greater concentrations normal orientation needs more energy. On approaching from the direction of small and great concentrations, the concentration at which the duration of saturation is independent of the temperature, a concentration can indeed be obtained at which the same energy is needed for normal as well as for abnormal orientation.

Thus recent investigations on the saturation of gelatineous dyestuffs, besides supporting the existence of the orientation effect, supply also important informations on the mechanism of the preexcitation effect.

Summary.

To what an extent the saturation of gelatineous dyestuffs depends on temperature was investigated. The main results were as follows:

1. The optimal concentration shifts with increasing temperature towards greater concentrations.

2. A concentration exists at which the duration of saturation is the same at every temperature.

3. At greater concentrations the normal, at small concentrations the abnormal orientation requires more energy.

Subsequently these investigations confirm the orientation of molecules, furnish also further informations on the mechanism of the preexcitation effect.

Acknowledgement. The author is indebted to the late Prof. P. Fröhlich director of the Experimental Physical Institute of the University of Szeged for his constant interest and suggestion.

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Institute of Experimental Physics

Connection Between Absorption and Emission of the Alcoholic Solution of Acridine Orange NO

By P. Szőr

Introduction.

P. Ramart, M. Gromez and M. Martynoff investigated the absorption of the acridine dyestuffs. (1). Particularly the absorption of the solid gelatine solution of acridine orange NO was studied by H. Mischung, (2) while P. Fröhlich and H. Mischung studied its emission (3). In this paper the emission and absorption of the alcoholic solution of acridine orange base was established.

The dyestuff acridine orange consists of two tautomer forms; which are in equilibrium, and are influenced by alkalis and acids. Under the influence of the former II., under that of the latter I. is predominant.

The object of the following investigations was to determine to which extent these tautometer forms participate in the establishment of the phenomena of fluorescence. For this reason acid or alkali, respectively, were added to influence the tautomer forms in the one or other direction.

Measurements.

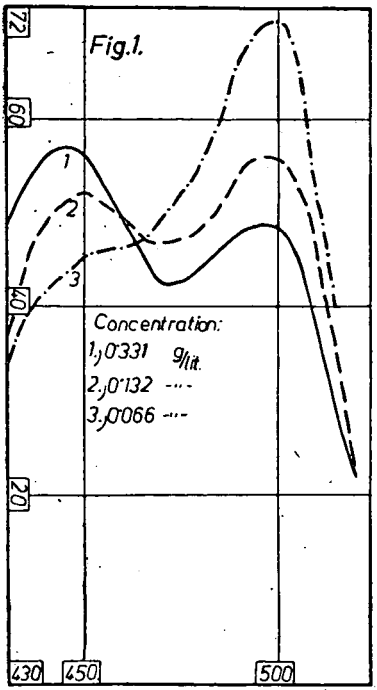
I. Measurements of absorption.

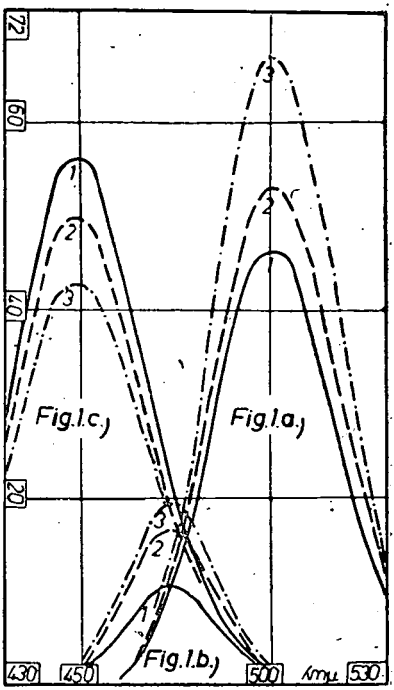
1. *Absorption of neutral solutions.*

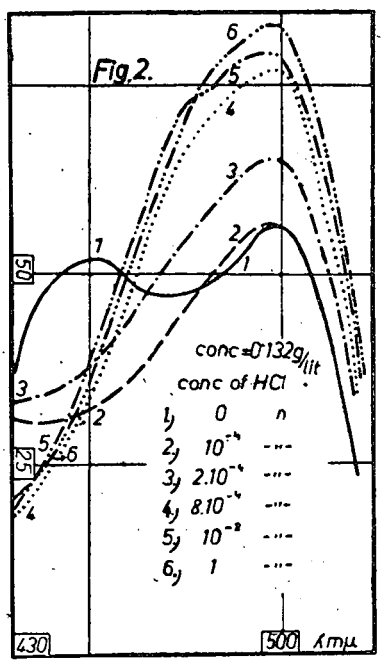
The alcoholic solution of the acridine orange base was investigated in three different concentrations, i. e. a concentration of $c = 331$ mg/lit, 132 mg/lit, and 66 mg/lit respectively. The absorption values were converted into a concentration of 3160 mg/lit. These absorption values are shown in Fig. 1. The figure displays two maxima. Thus it could be concluded that there are two partial bands, however, the analysis made by the method of Kiss and Sándorffy exhibited three partial bands (4). In this analysis the established maximum (λ_m) and the k distribution constants were considered to be as permanent within the same band, and concerning the other curves, the construction of the original curve with values λ_m and k; in alkaline and in acidified solutions was attempted. A similar method of analysis was employed by Gilbert N. Lewis, Theodor T. Magel, and David Lipkin, (5). On investigating the absorption curves they used the absorption curve of a highly diluted solution as base and a_m as unit, this basic curve was substracted from the other curves thus a new band was obtained.

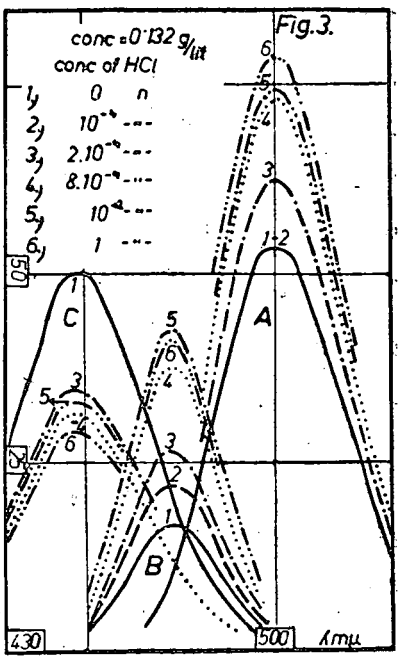
Fig. 1. shows the analysis of the alcoholic solution of the acridine orange base. The maxima of each band are 500, 473, and 448 $m\mu$. The k-values are 0,91, 0,75, and 1,2, respectively. This figure demonstrates that the maximum of band III diminishes with the decrease of the concentration, while that of bands II and I

below); with the aid of these λ_m and k-values the λ_m and k-values of band III were calculated from neutral solutions.







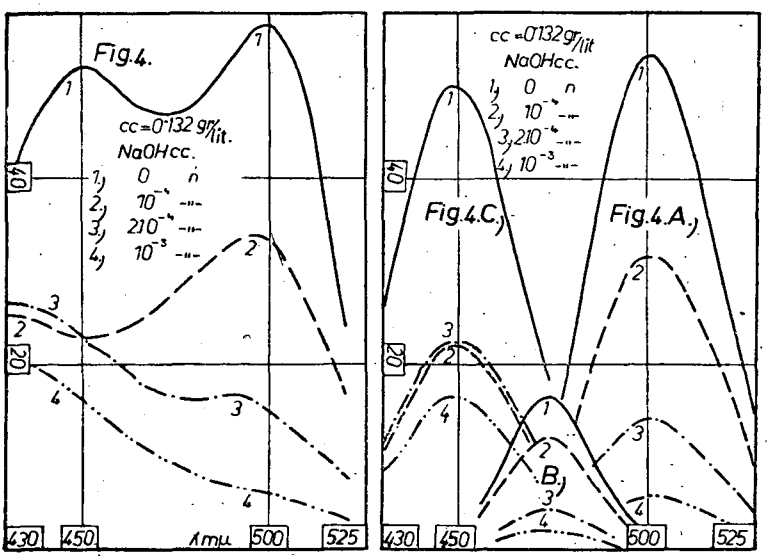


increases. The λ_m and k-values of bands I and II were established from the acidic solutions (as regards their absorption curves see

On adding the area of each partial band at each concentration, we find that the total of these areas agrees in all three cases within the limit of error. The area of a band is expressed by the formula $a_m k\sqrt{\pi}$ (4). Thus for a solution of concentration of c—331 mg/lit, $T = 117{,}6\sqrt{\pi}$ for that of $c = 132$ mg/lit, $T = 121.5\sqrt{\pi}$ and finally for that of $c = 66$ mg/lit, $T = 128.9\sqrt{\pi}$. Thus it is evident that changes in the concentration do not effect the relative number of the absorbing centres; but that they only are converted.

2. *Absorption of acidified solutions.*

The measurements were made in an acidified medium with a solution of $c = 132$ mg/lit Fig. 2. shows the absorption bands of these solutions and Fig. 3. the analysis. It can be seen that by increasing the concentration of HCL bands I and II also increase, while band III diminishes. When the concentration of the acid reaches 1,6 molecules HCL per dyestuff molecule, in spite of the very high increase in the concentration of HCL the absorption values scarcely change. This phenomenon may lead to the conclusion that if there are 1-2 molecules of HCL per 1 molecule of dyestuff, form I dominates, thus further molecules of HCL can have but a slight affect on the absorption, or equilibrium of dyestuffs.



3. *Absorption of alkaline solutions.*

Fig. 4. demonstrates the absorption bands — as measured in NaOH alcoholic solution of acridine orange base — and also the partial bands. Similarly to the acidified medium the three bands are also present, but in the solutions of greater concentrations band III is predominant. However, in acidified solutions band III is not enchanced on adding alkali, but diminishes, nevertheless as bands II and I decrease more than band III, the latter remains predominant.

On observing the absorption bands ranging between 440 and 430 $m\mu$ (see fig. 4.), in alkaline solutions a divergence between the analysis and the actually measured values can always be found. The same difference can also be observed in the neutral solutions of higher concentration. The acidified solutions on the other hand, do not show such differences. This seems to infer that by adding alkali a new maximum develops at the border of the ultraviolet and the visible spectrum. This subject was not investigated in detail.

On the addition of NaOH the size of the maxima of the partial bands decreased during the measurements. Therefore the solution were kept 1-2 days in daylight. By this time every band developed its definite form, which remained unchanged even under further excitation. All the measurements were made with such solutions. HCL and neutral solutions were exposed to the sun-light for as long as two months but no changes could be observed.

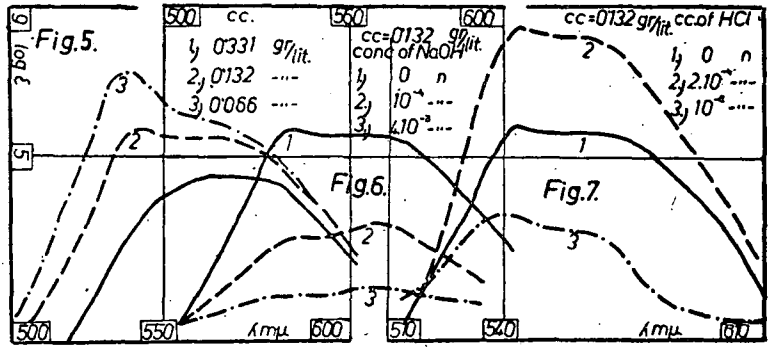
This phenomenon suggests the assumption that changes of the structure of acridine orange base in an alkaline medium cannot be ascribed solely to the effect of alkali but that the energy of light is also required.

II. Measurements of emission.

The emission of acridine orange base was also measured. The measurements were made with the spectral photometer of König—Martens. The intensity of the emission was compared with a Tungsten filament lamp of 12 Volt, 36 Watt, the spectral distribution of which was established with a photocell. The intensity of the emission in the figures is given in arbitrary units.

1. *Emission of neutral solutions.*

The fluorescence emission of three solutions of different concentration were measured. The concentrations of the neutral solutions were identical to that of the alkaline solutions. Fig. 5. shows



the spectral distribution of the emissions. It demonstrates the increasing of the emission at diminishing concentration although the emission values are not converted into concentration units. The figure demonstrates furthermore that with decreasing concentration the absorption at wave length 540 $m\mu$ increases considerably and shows a maximum, whereas the emission value remains almost unchanged at 565 $m\mu$.

2. *Emission of acidified solutions.*

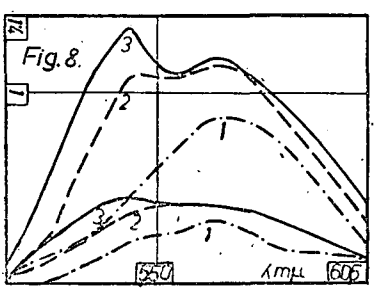
Figure 6. displays the result of the emissions of acidified selutions. As compared with neutral solutions, we cannot find any difference in the form of the emission curves, only the emission values differ. A small amount of HCL increases the emission, while a greater concentration of HCl diminishes it. On the other hand, HCL enhances the absorption, in spite of the fact of the absorption, value changing only to an insignificant extent above a certain HCL concentration. Till a certain HCL concentration is reached the emission increases, but on exceeding it diminishes. Thus there is a HCL concentration above which the absorbed energy is transformed in a slighter degree into emitted energy. The detailed investigation of this problem is in progress.

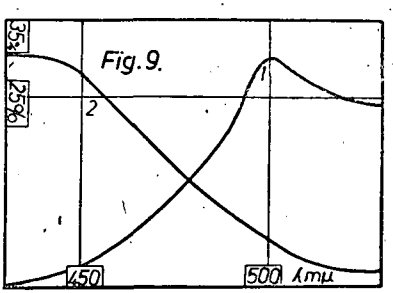
3. *Emission of alkaline solutions.*

On addition of alkali to alkaline solutions the emission and absorption diminish. It was established in connection with emission measurements that light exerts an effect on alkaline solutions. This is similar to the effect found for absorption, i. e. the emission decreases during excitation. Consequently the measurements were made in solutions which were exposed 1-2 days to sun-light after which the emission bands took up their final forms.

4. *Connection between absorption and emission bands.*

On observing the slight variations of the emission under the influence of HCL and alkali it can be stated that HCL enhances the band in the emission near 540 $m\mu$ (Fig. 6.), while in alkaline solutions the band near 565 $m\mu$ predominantes (Fig. 7.). Comparing these with the absorption bands we find that for acidified solutions in which the partial bands of absorption I and II predominate (Fig. 2.), the partial band of the emission near 540 $m\mu$ dominates. For alkaline solutions, where partial band III predominates (Fig. 4.), the partial band at 565 $m\mu$ is in prominence. It may be inferred therefore that the emission band at 540 $m\mu$ is caused by the absorption bands I and II and the emission band at 565 $m\mu$ by absorption band III. Consequently the emission of tautomer form I shows the band at about 540 $m\mu$ and that of tautomer form II the band near 565 $m\mu$.





In order to determine whether this supposition is correct the neutral solutions were excited through a filter. The results of the respective measuremnts are shown in Fig. 8. — Fig. 9. shows the transmissivity of the filters. Fiter *a)* transmits the part corresponding to absorption band I, and filter *b)* the part corresponding

to band III. The curves under *a)* demonstrate in Fig. 8 the emission, measured at the excitation with filter *a)*, and the curves under *b)* show the measurements with filter *b)*. Although apparently the transmissivity of both filters in bands I and III is almost identical the intensity of the emission curves differs greatly. The emission diminishes using filter *b)* to the same extent to which the transmissivity of the filter diminishes in absorption band I. Namely the area of the emission curve of solution 2. ($c = 132$ mg/lit) yields 1.74 units for excitation with filter *a)* and 0.56 units for filter *b)*. On the other hand, the transmissivity of filter *a)* amounts to 30 percent at 500 $m\mu$ and 7.5 percent for filter *b)*. The diminution of the transmissivity is fourfold, that of the emission 3.1 fold. On the base of this approximative calculation it can be postulated that the energy absorbed by absorption band I is transformed into emitted energy, i. e. tautomer form I emits.

In order to establish the emitting, tautomer form and the emssion band which corresponds to a certain absorption band the emission bands must be analysed.

Such an analysis had been already employed by P. Borissov (6). His method is in principle identical with the analysis of Kiss and Sándorffy (4), but for the fact of P. Borissov establishing the distribution of the emission value according to λ, while Kiss and Sándorffy employed ν for the establishment of the distribution of the absorption. In contrast to B. Borissov the analysis was attampted — similarly to the absorption according to ν.

This analysis may be carried out beyond 550 $m\mu$ i. e. the emission curve may be given by the formula

$$J = J_0 e^{-\left(\frac{\Delta\nu}{h}\right)^2}$$

The curve between 500 and 550 $m\mu$, particularly the ascending part of the curve, is so abrupt that the distribution function may not be employed. The divergence between the emission curve and the distribution function is explained by the fact that the absorption and emission bands cross each other, consequently the solution absorbs its emitted light, i. e. self-absorption occurs. The nearer the wave-length of the emitted light is to 500 $m\mu$, the greater is the self-absorption. Consequently, the smaller the measured emission relatively is, the greater is the self-absorption at the corresponding wave-length. Thus the measured emission decreases, by degrees towards the 500 $m\mu$, i. e. the steepness of the curve does not diminish according to the requirements of the distribution function but increases. Hence an attempt to analyse fails and the absorption and emission cannot be compared.

Summary.

The absorption and demission of the alcoholic solution of acridine orange NO was measured.

The absorption bands are composed of three partial bands. The changes of the partial bands in acidified and alkaline mediums and the comparison of the respective emission bands seem to point

to the fact that the fluorescence emission is caused by one of the tautomer forms of the dyestuff.

Owing to self-absorption an analysis of the emission bands could not be accomplished.

Acknowledgement. The author is indebted to late Prof. Paul Fröhlich for his kind interest and suggestions.

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Institute of Experimental Physics

About an Effect of Oriented Molecules on Polarized Light

By L. Szalay

Introduction.

According to the investigations of P. Fröhlich and L. Szalay the dyestuff molecules are oriented in rigid gelatineous solution of acridine orange under illumination(1). If a part of the solution is preexcited by polarized light and after the preexcitation the phosphorescence emission is measured by weak polarized light, at the same time illuminating also the unexcited part of the preparation, the intensity of emission of the preexcited surface is greater or smaller than the intensity of emission of the unexcited surface. When the directions of polarization of preexciting and exciting lights are parellel, the preexcited surface has a more intensive phosphorescence emission than that of its surroundings; when they are perpendicular, the phosphorescence emission of the preexcited surface is smaller than that of its surroundings.

The effect is similar to that found by G. N. Lewis and his co-workers (2), according to which the absorption of dyestuffs, exposed to and measured by polarized light, depends on the direction of polarization of the measuring light. The absorption is great when the directions of polarization of exciting and measuring lights are parellel, and small if they are perpendicular.

Both effects may be explained by assuming the orientation of molecules. Planar molecules have two optical axes which are perpendicular. The molecule is excitable if its plane is perpendicular to the beam, and if, when excited with polarized light, one of its axes is parallel to the direction of polarization. During preexcitation the molecules are oriented until the plane of their optical axes is normal to the beam of light and one of their optical axes takes up a parallel position to the direction of polarization. Mischung was the first to prove that the absorption coefficient increases during excitation, this establishment indicates the existence of an orientation effect (3).

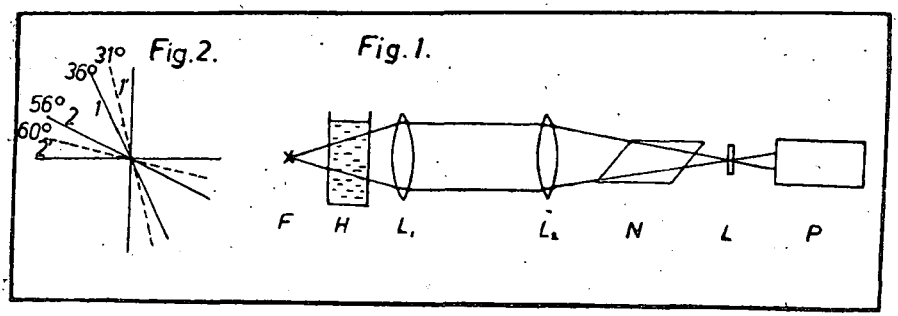
The phenomenon of saturation which means that the phosphorescence emission requires considerable time to reach its maximum during excitation is also interpretable by assuming the orientation of the molecules (4).

The preexciting effect proves that the oriented state due to irradiation persists in gelatineous solutions also after discontinuing the irradiation, consequently the molecules are permanently oriented in rigid gelatineous solutions.

The orientation effect is undoubtedly a phenomenon which is due to the reciprocal effects of light and dyestuff molecules caused by the influence of light on the molecules. It is obvious that the permanently oriented molecules must exert an influence on polarized light. This effect is described in the following paper.

Experimental.

It was demonstrated that oriented molecules influence the direction of the polarization of light. As was described above in a rigid gelatineous solution, the permanently oriented state may be caused by excitation with intense polarized light. The observations were made with a Cornu-polarimeter to ascertain the direction of polarized light after it had passed through the preexcited dyestuff solution. Considering that the measuring light itself also exerts an orientation effect on the molecules, its intensity must be very small as compared with the intensity of the preexciting light. Thus the intensity of the preexciting light had to be reduced by means of a glass-plate covered with lamp-black on using it as measuring light. Fig. 1. exibits the measuring arrangement.



The source of light „*F*" was a 5000 watt tungsten filament lamp. The light from passes through a circulating water cooler

(H) and two lenses (L_1 and L_2). The polarized light is produced by means of a nicol (N). The direction of polarization is measured with a polarimeter (P). The course of the measuring was as follows. The plate was illuminated 10 minutes with intense polarized light. This time is sufficient to induce permanent orientation. Subsequently the intensity of light was decreased by means of a glass-plate covered with lampblack. The direction of polarization was changed through rotating the nicol, and the angle of rotation was measured with the polarimeter. First the rotation angle was measured on removing the gelatine plate placed between the polarimeter and nicol, then the plate was put between the nicol and polarimeter, and the rotation angle measured again.

Results.

The first results disclosed that not only light exerts an orientating effect on the molecules, but that also the oriented molecules affect polarized light, the direction of polarization of the faint light after transmission through the solution rotates if the solution contains oriented molecules. Detailed investigations gave very interesting results. Hence it was obvious that the angle of rotation depends to a great extent on the difference between the direction of polarization of the orientating light and that of the weak measuring light. The results are summarized in Table I referring to a rigid gelatineous plate of 0.1 mm. The preparation contained acridine orange.

Table II.

Direction of polarization without plate	Direction of polarization after the introduction of the plate	angle of rotation
0°	0°	0°
18°	16°	2°
26°	23°	3°
36°	31°	5°
56°	56°	—4°
66°	69.5°	—3.5°
75°	76°	—1°
90°	90°	0°

The concentration of the dyestuff was $10^{-2,5}$ gr dyestuff/cm³ dry gelatine. The measurements were made at room-temperature. The orientation was made with nicol at 0°, the light polarizing horizontally. Table I shows that the direction of polarization remains unchanged on passing through the plate if the weak polarized measuring light is also horizontally polarized. But if the direction of polarization of measuring light is changed, the preparation containing oriented molecules rotates to a certain degree the direction of polarization of the light passing through it. The direction of polarization will be rotated to a lesser extent after transmission through the dyed plate comprising oriented molecules./e. g. if the nicol is at 18° on the light passing through the plate it will be

reduced to 16°. In other words, the oriented molecules rotated the direction of polarization as if they wanted to change the direction back to that originally employed for orientation. This behaviour could, however, only be observed to an angle of 36°. At an angle of 56° a change in opposite direction took place. On introduction of the plate containing the oriented molecules at this angle the direction of polarization rotated towards the opposite direction. However, the molecules had no influence whatever on the direction of polarization if the measuring light polarized vertically (Fig. 2.).

The two perpendicular directions correspond to the horizontally and vertically polarized directions respectively. The plate rotates direction 1 of polarized light to direction 1′, and direction 2 of polarized light to direction 2′ respectively. The direction of the two perpendicularly polarized lights does not change when it passes through the plate.

Several plates of various concentration and thickness were investigated and similar results were always obtained. Since all examined preparations behaved essentially in the same manner, only differing in the angles of rotation, it does not seem necessary to enumerate further data.

It should further be noted that the method employed was unsuitable for the determination of the angle between 0°, and 90° dividing the two directions of rotation. Therefore the change in the direction of polarization was simply observed by means of a nicol. The well-known phenomenon, that the linearly polarized light becomes partially polarized on passing through the gelatine plate was observed. The rotation which was measured with the polarimeter is not the rotation of the plane of polarization, but that of the plane of the partial polarization.

Summary.

If was demonstrated by the aid of the preexciting effect that oriented molecules influence the direction of polarized light. One of the optical axes of the oriented molecules is parallel to the direction of the polarization of the exciting light, the other is perpendicular. If a weak polarized light is passed through a dyestuff solution which contains oriented molecules the direction of polarization will be rotated in the direction of the axis which is closer to the direction of polarization.

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Institute of Experimental Physics

A New Method for the Demonstration of Self-Excitation

By L. Szalay and L. Szőllősy

Introduction.

On dealing with investigations concerning Lenard phosphors different authors suggest the possibility of self-excitation. This means that the phosphor can be excited by light of its own emission. In most cases the process of self-excitation was only assumed, but could not be proved.

Riehl (1) was the first to establish self-excitation by a direct method in a series of tedious experiments. He found that the self-excitation was slight. In phosphor mixtures self-excitation can also be excepted if the emission band of one of the components and the absorption band of the other have a common area. Such self-excitation was also observed in the case of Lenard phosphors (2).

As regards gelatine phosphors self-excitation can be theoretically assumed. P. Fröhlich and H. Mischung have shown that the emission band (3) and absorption band (4) of acridine orange have a common area. Taking into account the very slightness of the the intensity of the phosphorescence emission, as compared with the usual intensity of exciting light, and on the other hand that only a small part of the emission band is absorbed, only a very slight self-excitation effect can be expected.

Self-absorption was also experimentally proved by G. N. Lewis and his co-workers (5). Concerning the analysis of the emission band of fluorescence P. Szőr also considered the possibility of self-absorption (6). Recently P. Fröhlich and P. Szőr elaborated a method for the calculation of the emission band freed from self-absorption (7).

According to prévious investigations of one the authors the existence of self-excitation was presumed (8). During the measuring of the time of the saturation half of the preparation was covered by means of a screen and the other half was saturated. After the removal of the screen the time needed for the disappearance of the distinct boundary line dividing the saturated and unsaturated sections was measured. It could be observed that the non-pre-excited surface does not exhibit a uniform light distribution during excitation, but lightens from the boundary line towards the border. It can be assumed that the phosphorescence emission of the molecules on the border of the dark surface encreases the intensity of the exciting light, consequently the dark surface close to the boundary line is saturated first.

In this paper a method has been elaborated concerning the direct determination of self-excitation in the case of rigid phosphorescent gelatine solutions which have an extremely short time of decay; at which it was not possible to apply Riehl's method.

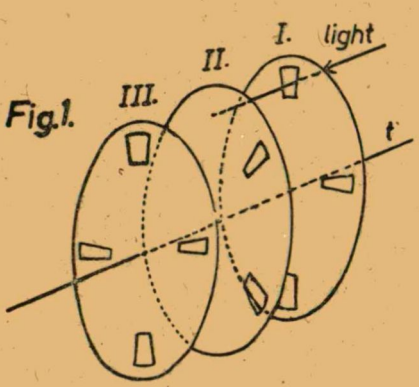
A rigid gelatine solution of acridine orange was used. The solution had a concentration of $10^{-2,25}$ gr dyestuff (cm^3 dry gelatine. The preparations were made by the method of P. Frőlich (9).

The thickness of the plate was 0.1 mm.

Method and Results.

For the direct determination of self-excitation the Bequerel phosphoroscope (10) was modified.

On the axis (*t*) of the two discs (I. II.) of the phosphoroscope a third disc (III.) also having 4 openings was adjusted (Fig. 1). The discs were placed into a cylinder shaped metal case each of the two oppositely situated walls having an opening at the height of the opening of the disc. The discs were situated on the axis at a distance of about 3 cm. Thus the gelatine plates could be placed between discs I, II and II, III. The gelatine plates were mounted on a metal frame fitting into two openings of the upper part of the cylindrical case.



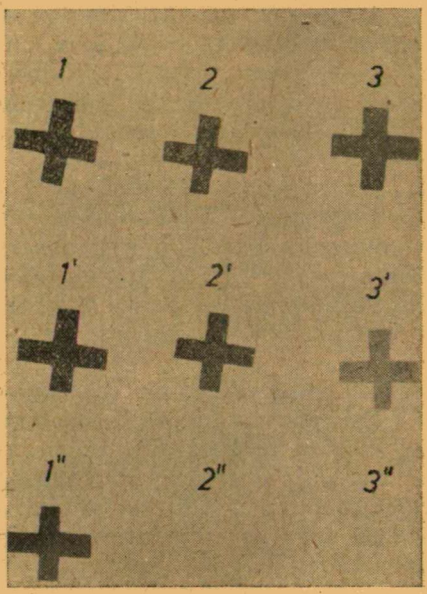


Fig. 2.

Into this phosphoroscope 2 pieces, cut out of the same plate, were inserted. If the phosphoroscope was in the position shown in Fig. I. the exciting light excited the preparation placed between discs I. II., but could not reach either the space between discs II. III. or the observer in front of disc III. If the rotating discs described an angle of 90° the phosphorescence emission of the plate placed between discs I. II. excited the preparation inserted between discs II. III.

However, the light could not yet reach the observer. After a made an angle of 90° the phosphorescence emission of the plate placed between discs I. II. could not reach the space between discs II. III, but the phosphorescence emission of the plate inserted between discs II. III. previously excited by self-excitation could be observed through the opening of disc III.

Thus on rotating the phosphoroscope the phosphorescence emission due to self-excitation can continually be observed through the opening of disc III.

As was already mentioned the energy needed for self excitation is very slight. Therefore the phosphorescence emission caused by self-excitation could not be visually observed.

The preparation placed between discs I. II. was excited by means of a tungsten filament lamp of 1000 W. and the self-excitation was observed photographically. A camera was adjusted in front of the opening of disc III. and the photographic plate covered with a black paper having a cross-shaped slit. The occurence of self-excitation was established through the blackening of the plate on the area of the slit.

The whole apparatus was carefully constructed enabling the light only to reach the photographic plate from the self-excited preparation. Yet to ascertain if the blackening is not after all caused by the dissipated light, or if the preparation between discs II. III. is not excited by it, the photographie plate was exposed under the same conditions, to the light coming from the opaning of disc III. in the following cases.

1. Pure gelatine was placed between discs I. II. and also between II. III.

2. Pure gelatine was inserted between discs I. II., and a gelatine dyestuff solution between II. III.

3. Gelatine dyestuff solution was put between discs I. II and II. III.

The blackening caused by the dissipated light is shown in Fig. 2. picture 1., picture 2. demonstrates the effect of the dissipated light and the excitation caused by it, finally picture 3. the blackening caused by the dissipated light and the excitation effected by it and the phosphorescence due to excitation.

Orthochromatic „Forte" plates sensitized particularly for green were used, the experiments showed that after three hours exposure a satisfactory blackening was obtainable.

Three series of pictures were made under the conditions mentioned above, Fig 2. shows each of the series in a row. The crosses denoted with 1, 2, 3, belong to the first series. Picture 1 was taken with gelatine dyestuff solution, picture 2 with pure gelatine and gelatine dyestuff solution, picture 3 with pure gelatine between the discs.

Fig. 2. demonstrates well that picture 1 exhibits the greatest extent of blackening which was also caused by self-excitation. In the second series (1′, 2′, 3′,) the same can be observed. In the case of the third series picture 1″ shows blackening, indicating that only the phosphorescence emission caused by self-excitation reached the photographic plate. This was attained by reducing the area of the opening to 1 cm², thus eliminating more completely the dissipated light. Picture 2″ and 3″, on which there is no blackening, were also taken with a 3 hours exposure. Hence cross 1″ is exclusively produced by the phosphorescence emission caused by self-excitation.

Of course all the pictures belonging to the same series were made under the same conditions i. e. the same photographic plate, exposure and development were applied.

Summary.

A new and rapid photographic method for the establishment of self-excitation was elaborated which can also be applied to objective measurements. Self-excitation was shown in the case of rigid gelatine solution of acridine orange.

The measurements were made at the Physical Institute of the University of Szeged.

Acknowledgement.

Authors are very indebted to the late Prof. P. Fröhlich for his kind interest and advice.

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On the Structure of Gelatine

By L. Szalay and J. Grasselly

Introduction.

Many investigators have dealt with the structure of gelatine approaching the problem from the chemical and physical point of view. According to earlier investigations carried out with *X*-rays no crystal interference could be observed. Two diffuse fringes were found, hence it was established that gelatine is a mixture of two amorphous substances (1). Further roentgenographic examination showed the *X*-ray diagram of gelatine to have a typically broad fringe, surrounded by another distinct one characteristic of crystal interference. A second diffuse ring can also be observed (2). On stretching the gelatine the diffuse fringe characterising the amorphous state changes and resembles the distinct interference ring.

It was assumed that in a normal state gelatine is probably a crystalline substance possessing a very disordered structure having, however, periodicity in one direction. On the other hand, it was also suggested that the distinct fringe is caused by parallel elements but not by a lattice structure.

The occurence of a fringe characterising crystalline interference was shown by different investigations (3). Several authors have stated that gelatine has a crystalline structure, or that at least besides the amorphous modification it contains also undoubtedly crystalline ones, consequently gelatinization means crystallization.

However, on the base of the roentgenodiagram some authors come to the conclusion that gelatine consists of highly polymerized components, probably of amino acid chains which interlace in a sponge like manner. In the holes of the sponge a less amorphous form can be found (5).

On the base of later investigations the conception of gelatine chains having under certain circumstances an almost perfect lattice structure arrangement became preponderant (6). Several authors also made an attempt to determine on the base of the diagrams the size of the elementary cell (7, 8, 9). In this relation the recorded data diverge considerably. According to one author the crystal lattice of collagen is monoclinic and both the collagen and gelatine are roentgenographically identical (9).

According to Clark there is no satisfactory interpretation for the crystal structure, nevertheless, concerning a collagen compound, the orthorhombic form of its crystal lattice could be established (8). The transition point of gelatine was found to vary, this fact was interpreted by the assumption of the crystals varying in size (10), which probably is also the cause of the divergence of the data recorded by different authors as to the size of the unit cell.

Results.

At the experiments dealing with fluorescence and phosphorescence carried on at our institute the dyes were dissolved in a gelatineous solution. After solidification of the solution the behaviour of the dry gelatineous dyestuff solution was investigated. Naturally pure gelatine was also examined from different points of view (11).

On preparing the preparation the gelatine is dissolved in hot water and the solution is poured on to a mercury surface, from which it can be easily removed after solidification in the form of a thin plate (12). The plates used for the investigations were 0.1—0.3 mm. thick. The ash content of the gelatine was 2.10 per cent.

On examining the preexcitation effect there seemed to be a possibility to explain it by the orientation of molecules (13). The researches relating to the preexcitation effect revealed that the intensity of the emission excited by polarised light depends on the direction of the polarization of the preexciting light. In connection with these investigations it was found particularly necessary to examine the optical behaviour of gelatine concerning polarized light.

Above all it seemed desirable to establish the well known anisotropic character of the gelatine layer. The plate was examined under a polarisation microscope between crossed nicols. As expected on each revolving of the object-table darkening, resp. lightening could be observed four times. The extinction was, however, not complete.

On examining the preparations under the polarisation microscope between crossed nicols an interesting phenomenon could be observed. Not quite perfect plates exhibited at several points bubbles which were also visible to the naked eye. On examining them between parallel nicols they did not exhibit any particular characteristics, however, on investigating them between crossed nicols, an interference figure appeared resembling that induced by biaxial crystals under conoscope. Under the orthoscope — on examining with parallel beams of light — no interference figure could be observed. Investigating the parts of the plate not demonstrating bubbles the phenomenon mentioned above could not be seen. Under the orthoscope on the other hand, the points containing bubbles showed the interference figure. This phenomenon could only be explained by assuming the bubbles to behave as a converging optical lense thus modifying the orthoscope into a conoscope. Therefore if our assumption was correct the points not revealing bubbles had also to show the interference figure under the conoscope.

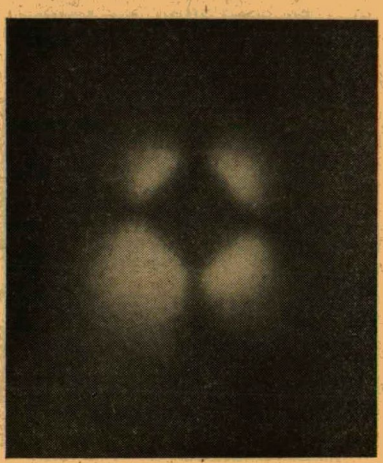

Fig. 1.

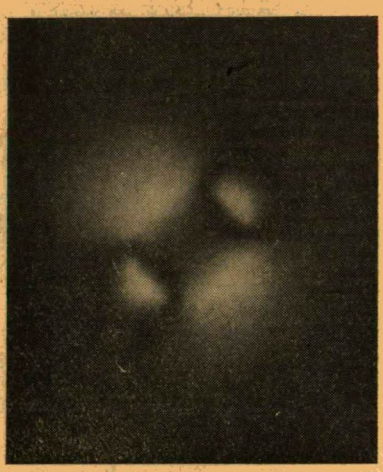

Fig. 2.

The investigations proved the correctness of this supposition. Under the conoscope the interference figure exhibited on photos No 1.2 could be obtained from every point of the plate. If the axial plane, i. e. the plane including the two optical axes lies parallel to the direction of vibration of the polariser, Fig. 1 shows the interference figure. If, however, these two directions are inclined at an angle of 45° the figure is like that shown on Fig. 2.

It can therefore be stated that rigid gelatine behaves like a biaxial crystal, or that at least of its two forms — amorphous and crystalline — the latter has a biaxial crystal structure.

Hitherto the roentgenograms did not offer a decisive solution of this problem.

According to one author the roentgenodiagram of collagen indicates that the crystal system is monoclinic and according to another it is rhombic, they also assert the roentgenographic identity

of gelatine and collagen. The researches mentioned above refer to gelatine. Our investigations did not either yield an accurate definition of the crystal system. However, it could undoubtedly be proved — in accordance with the results of other investigators — that the crystal modification of gelatine behaves like a biaxial crystal.

As regards the optical character of the crystal employing a 1.0. gypsum plate the substraction was found to be parallel to the direction of the smallest elasticity of the gypsum plate, consequantly the gelatine crystals are of negative optical character. Fig. 2. indicates that the optical axes are close to each other, therefore the bisector of the acute angle is probably perpendicular to the plane of the plate.

Some investigations were also carried out concerning the modifications of the structure during solidification. The dilute solution did not exhibit anisotropy. The same refers to the state of the solution which has not yet undergone solidification, which fact undoubtedly supports the establishments of Derksen and Katz as well as those of Sokolov (4). Namely according to Sokolov a 10 per cent gelatine gel exhibits a very distinct crystal interference fringe, a 10 per cent gelatine sol a less distinct one, whereas the highly dilute 1 per cent sol showes only an amorphous fringe. Recent investigations prove that the interference fringes obtained on gelation can be explained by an orientation process and not by crystallization which was also established by Sokolov. On solidification, however, a definite crystal structure is formed, an anisotropy of high degree can be observed, and the interference figure appears.

As the characteristic interference figures can be obtained on any section of the plate it is evident that its behaviour is uniform and that during solidification a regular arrangement takes place (5).

Further investigations are in progress.

Summary.

The structure of solid, dry, 0.1—0.3 mm. thick gelatine layers was investigated. The most important results are as follows:

1. The layers possess only in rigid state a crystal structure. After solidification the whole plate has a uniformly anisotropic character.

2. The crystalline form of gelatine undoubtedly behaves like a biaxial crystal, consequently it belongs to either the rhombic, the monoclinic or the triclinic sytem. The crystal has an optically negative character.

3. The axial plane of the crystal is perpendicular to the plane of the gelatine layer.

4. The direction of the greatest elasticity is perpendicular to the plane of the gelatine layer.

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